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(Rev. 5-93)

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

ATTORNEY'S DOCKET NO **H3815 PCT/US**

U.S. APPLICATION NO. (if known sec 17 CFR 1.5)

09/868549

INTERNATIONAL APPLICATION NO.
PCT/EP99/09739

INTERNATIONAL FILING DATE
December 10, 1999

PRIORITY DATE CLAIMED
December 19, 1998

TITLE OF INVENTION

TENSIDE GRANULATES

APPLICANT(S) FOR DO/EO/US

Ditmar Kischkel, Manfred Weuthen, Jutta Stute, and Stefan Podubrin

Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☒ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). (UNEXECUTED)
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment
 - ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☐ Other items or information.:

"Express Mail" mailing label number **EL541613148US**

U.S. Application No. (If known see CFR 1.30) <div style="font-size: 24pt; font-weight: bold;">09/868549</div>		INTERNATIONAL APPLICATION NO. PCT/EP99/09739		ATTORNEY'S DOCKET NUMBER H3815 PCT/US	
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17. ■ The following fees are submitted: Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO..... \$860.00 International preliminary examination fee paid to USPTO (37CFR 1.482) \$690.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37CFR 1.445(a)(2)).... \$760.00 Neither international preliminary examination fee (37CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO. \$1000.00 International preliminary examination fee paid to USPTO (37CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)..... \$96.00				CALCULATIONS PTO USE ONLY	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$	860 00
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date 37 (CFR 1.492(e)).				\$	
Claims	Number filed	Number Extra	Rate		
Total Claims	14 - 20 =	0	X 18.00	\$	0 00
Independent Claims	3 - 3 =	0	X 80.00	\$	0 00
Multiple dependent claims (s)(if applicable) 0			+ 260.00	\$	0 00
TOTAL OF ABOVE CALCULATIONS =				\$	860 00
Reduction by ½ for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL =				\$	860 00
Processing fee of \$130.00 for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37CFR 1.492(f)).....				\$	
TOTAL NATIONAL FEE =				\$	860 00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
TOTAL FEES ENCLOSED =				\$	860 00
				Amount to be: refunded	\$-----
				charged	860.00

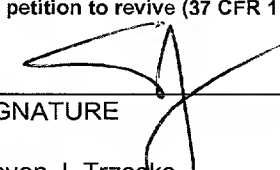
a. ☐ A check in the amount of \$_____ to cover the above fees is enclosed.

b. ■ Please charge my Deposit Account No. 50-1177 in the amount of \$ **860.00** to cover the above fees.
 A triplicate copy of this sheet is enclosed. Order No. 01-0373.

c. ■ The Assistant Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
 overpayment to Deposit Account No. 50-1177. A triplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must
 be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO: Cognis Corporation, Law Dept.
 2500 Renaissance Blvd., Ste. 200
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 Steven J. Trzaska
 NAME ATTORNEY FOR APPLICANT
 36,296
 REGISTRATION NUMBER

"Express Mail" mailing label number EL541613148US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Kischkel et al.
I.A. Number : PCT/EP99/09739
I.A. Filing Date: December 10, 1999
Priority Date : December 19, 1998
Title : TENSIDE GRANULATES

Grp./A.U. : Unknown
Examiner : Unknown

Docket No. : H 3815 PCT/US

Assistant Commissioner for Patents
Box PCT
Washington, DC 20231

ATTN: DO/EO/US

PRELIMINARY AMENDMENT

Sir:

Preliminary to examination, please amend the instant application as follows.

In the Specification:

At page 1, line 1, delete "Field of the Invention", and insert
--Background of the Invention--.

At page 1, line 7, delete "Prior Art".

Enter a new page 20, submitted herewith, containing the Abstract of the
Disclosure.

In the Claims:

Cancel claims 1-9, without prejudice.

Please enter the following new claims.

10. A surfactant composition comprising:
- (a) from about 75 to 97% by weight of a fatty alcohol sulfate; and
 - (b) from about 3 to 25% by weight of an olefin sulfonate, all weights being based on the total weight of the composition, and wherein the composition is in granular form.

**Preliminary Amendment of U.S. National Stage for International Application
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11. The composition of claim 10 wherein the fatty alcohol sulfate is present in the composition in an amount of from about 85 to 95% by weight, based on the weight of the composition.

12. The composition of claim 10 wherein the olefin sulfonate is present in the composition in an amount of from about 5 to 15% by weight, based on the weight of the composition.

13. The composition of claim 10 wherein the fatty alcohol sulfate corresponds to formula I:



wherein R^1 is a linear or branched, saturated or unsaturated hydrocarbon radical containing from about 6 to 18 carbon atoms, and X is an alkali metal or alkaline earth metal, ammonium, alkyl ammonium, alkanolammonium or glucammonium.

14. The composition of claim 10 wherein the olefin sulfonate is derived by:

(a) addition of SO_3 onto an olefin corresponding to formula II:



wherein R^2 and R^3 , independently of one another, represent H or alkyl groups containing from 1 to about 20 carbon atoms, with the proviso that R^2 and R^3 together contain at least 6 carbon atoms;

(b) hydrolysis; and

(c) neutralization.

15. The composition of claim 10 wherein the olefin sulfonate comprises:

(a) ca. 60% by weight of alkane sulfonate; and

(b) ca. 40% by weight of hydroxyalkane sulfonate of which 80 to 85% by weight are monosulfonate and 15 to 20% by weight are disulfonate.

16. A process for making surfactant granules comprising:

(a) providing an aqueous paste containing a fatty alcohol sulfate;

(b) providing an olefin sulfonate; and

(c) simultaneously drying and granulating the fatty alcohol sulfate and olefin

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sulfonate.

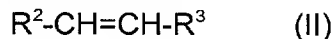
17. The process of claim 16 wherein the fatty alcohol sulfate corresponds to formula I:



wherein R^1 is a linear or branched, saturated or unsaturated hydrocarbon radical containing from about 6 to 18 carbon atoms, and X is an alkali metal or alkaline earth metal, ammonium, alkyl ammonium, alkanolammonium or glucammonium.

18. The process of claim 16 wherein the olefin sulfonate is derived by:

(a) addition of SO_3 onto an olefin corresponding to formula II:



wherein R^2 and R^3 , independently of one another, represent H or alkyl groups containing from 1 to about 20 carbon atoms, with the proviso that R^2 and R^3 together contain at least 6 carbon atoms;

(b) hydrolysis; and

(c) neutralization.

19. The process of claim 16 wherein step (c) is performed in a fluidized bed.
20. A cleaning composition containing the surfactant composition of claim 10.
21. The composition of claim 18 wherein the surfactant composition is present in an amount of from about 0.1 to 30% by weight, based on the weight of the cleaning composition.
22. A process for enhancing cold water solubility of a composition containing a fatty alcohol sulfate comprising adding an olefin sulfonate to the composition.
23. The process of claim 20 wherein the olefin sulfonate is combined with the fatty alcohol sulfate in an amount of from about 3 to 25% by weight, based on the weight of the composition.

REMARKS/ARGUMENTS

Claims 10-23 are currently pending in the instant application.

The Specification has been amended to include the preferred section headings pursuant to 37 C.F.R. §1.77. An Abstract of the Disclosure in accordance with the abstract of the corresponding international publication has been added on a separate sheet following the claims. All of the amendments to the Specification constitute deletions of original section headings and/or paragraphs, and insertions or additions of new section headings and/or paragraphs. It is submitted that the amendments to the Specification made herein introduce no new matter. Their entry is therefore proper and respectfully requested. Accordingly, pursuant to 37 C.F.R. §1.121(b)(1)(iii), no separate page captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE" is necessary.

Original claims 1-9 have been canceled and replaced with new claims 10-23 solely for the purpose of improving clarity and grammar, which may suffer in translation, and not for any reason which relates to the statutory requirements for a patent. New claims 10-23 have not been added in response to any rejection, nor in anticipation of any rejection. Applicant(s) respectfully submit(s) that the scope of new claims 10-23 corresponds to the scope of original claims 1-9, and that new claims 10-23 are no narrower than original claims 1-9. Furthermore, although a moot point in view of their cancellation, Applicant(s) respectfully submit(s) that original claims 1-9 satisfied the requirements of 35 U.S.C. §112, as filed. New claims 10-23 are supported by the claims as originally filed and by the Examples. No new matter has been introduced. Entry is therefore proper and respectfully requested.

**Preliminary Amendment of U.S. National Stage for International Application
PCT/EP99/09739 filed December 10, 1999**

Prompt examination of the instant application in view of the
amendments made herein is respectfully requested.

Respectfully submitted,



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Attached:

1. Added Page 20

Abstract of the Disclosure

A surfactant composition containing: (a) from about 75 to 97% by weight of a fatty alcohol sulfate; and (b) from about 3 to 25% by weight of an olefin sulfonate, all weights being based on the total weight of the composition, and wherein the composition is in granular form.

Tenside Granulates

Field of the Invention

This invention relates to surfactant granules of fatty alcohol sulfates and olefin sulfonates, to a process for their production and to the use of olefin sulfonates for improving the solubility of fatty alcohol sulfate granules in cold water.

Prior Art

Anionic surfactants, more particularly alkyl sulfates or fatty alcohol sulfates, are important constituents of laundry detergents, dishwashing detergents and cleaners. In the process used to produce them, anionic surfactants are obtained in the form of water-containing pastes with water contents of 30 to 75% by weight. In order to obtain solid products, the water-containing pastes are dried, for example in spray-drying towers, or are produced by drying and simultaneous granulation, more particularly in a fluidized bed. It is known, for example from European patent **EP 0603207B**, that water-containing pastes of alkyl sulfates can be converted into granules of high bulk density by drying and simultaneous granulation in a continuous fluidized bed. It is also possible in this process to incorporate inorganic or organic carrier materials.

$C_{16/18}$ fatty alcohol sulfate granules produced by simultaneous drying and granulation show inadequate solubility and dispersibility at low temperatures. Since the solution to this problem is very important for cold washing processes, the problem addressed by the present invention was to improve the dissolving and dispersing behavior of granular $C_{16/18}$ fatty alcohol sulfates at low temperatures.

Description of the Invention

The present invention relates to surfactant granules consisting of

(a) 75 to 97% by weight, preferably 85 to 95% by weight of fatty alcohol sulfates and

(b) 3 to 25% by weight, preferably 5 to 15% by weight of olefin sulfonates,

with the proviso that the quantities add up to 100% by weight.

The present invention also relates to a process for the production of surfactant granules in which a water-containing paste of component (a) is simultaneously dried and granulated in the presence of component (b). In

another embodiment, the invention relates to the use of olefin sulfonates in quantities of 3 to 25% by weight for improving the solubility of fatty alcohol sulfate granules in cold water.

It has surprisingly been found that, even in small quantities, olefin sulfonates improve the dissolving and dispersing behavior of granular C_{16/18} fatty alcohol sulfates, even at low temperatures. Accordingly, it is of advantage to use olefin sulfonate/fatty alcohol sulfate granules for low-temperature washing processes.

Fatty alcohol sulfates

Fatty alcohol sulfates which form component (a) are understood to be alkyl sulfates corresponding to formula (I):



(I)

in which R¹ is a linear or branched, saturated or unsaturated hydrocarbon radical containing 6 to 18 carbon atoms and X is an alkali metal or alkaline earth metal, ammonium, alkyl ammonium, alkanolammonium or glucammonium. Fatty alcohol sulfates are known anionic surfactants which are preferably obtained by sulfation of native fatty alcohols or synthetic oxoalcohols and subsequent neutralization. Typical examples of fatty

alcohol sulfates are the sodium salts of sulfation products of caproic alcohol, caprylic alcohol, 2-ethyl hexyl alcohol, capric alcohol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, linolyl alcohol, linolenyl alcohol and elaeostearyl alcohol and the technical mixtures thereof obtained, for example, in the high-pressure hydrogenation of technical methyl esters based on fats and oils or aldehydes from Roelen's oxo synthesis and as monomer fraction in the dimerization of unsaturated fatty alcohols. Fatty alcohols containing 12 to 18 carbon atoms and more particularly 16 to 18 carbon atoms are preferably used. Typical examples are technical fatty alcohol sulfates.

Olefin sulfonates

The granules according to the invention contain as a further constituent (b) olefin sulfonates which are normally obtained by addition of SO₃ onto olefins corresponding to formula (II):



in which R² and R³ independently of one another represent H or alkyl groups containing 1 to 20 carbon atoms, with the proviso that R² and R³ together contain at least 6 and preferably 10 to 16 carbon atoms, and subsequent hydrolysis and neutralization. Particulars of their production and use can be found in a synoptic article published in **J. Am. Oil. Chem. Soc.** 55, 70 (1978).

Internal olefin sulfonates may be used although α-olefin sulfonates which are obtained where R² or R³ is hydrogen are preferably used. Typical examples of the olefin sulfonates used are the sulfonation products obtained by reacting SO₃ with 1-, 2-, 3-, 4-octene, 1-, 2-, 3-, 4-, 5-decene, 1-, 2-, 3-, 4-, 5-, 6-dodecene, 1-, 2-, 3-, 4-, 5-, 6-, 7-tetradecene, 1-, 2-, 3-,

4-, 5-, 6-, 7-, 8-hexadecene, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-octadecene, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-eicosene and 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10- and 11-docosene. The sulfonation is followed by hydrolysis and neutralization, after which the olefin sulfonate is present in the mixture as
5 an alkali metal, alkaline earth metal, ammonium, alkyl ammonium, alkanolammonium or glucammonium salt and preferably as a sodium salt. The hydrolyzed α -olefin sulfonation product, i.e. the α -olefin sulfonates, advantageously consists of ca. 60% by weight of alkane sulfonates and ca. 40% by weight of hydroxyalkane sulfonates, of which 80 to 85% by weight
10 are monosulfonates and 15 to 20% by weight disulfonates.

Both olefin sulfonates in the form of water-containing pastes, for example sodium olefin sulfonate (C_{14-16}), Elfan® OS 46 A (Akzo Nobel), and water-free products, for example sodium olefin sulfonate (C_{14-16}), Elfan® OS 46 P (Akzo Nobel), may be used.

15 The present invention also relates to a process for the production of the surfactant granules claimed in claim 1 in which a water-containing paste of component (a) is simultaneously dried and granulated in the presence of component (b).

20 SKET granulation

A preferred possibility is to subject the water-containing surfactant paste to so-called SKET granulation. SKET granulation is understood to be a simultaneous granulation and drying process preferably carried out in batches or continuously in a fluidized bed. To this end, a water-containing
25 paste of component (a), for example a 30 to 65% by weight surfactant paste, and component (b) are introduced simultaneously or successively into the fluidized bed through one or more nozzles. If component (b) is present as a solid, it is advisable to introduce it into the fluidized bed through a solids metering unit. Preferred fluidized-bed arrangements have
30 base plates measuring 0.4 to 5 m. The SKET granulation is preferably

carried out at fluidizing air flow rates of 1 to 8 m/s. The granules are preferably discharged from the fluidized bed via a sizing stage. Sizing may be carried out, for example, by means of a sieve or by an air stream flowing in countercurrent (sizing air) which is controlled in such a way that only

5 particles beyond a certain size are removed from the fluidized bed while smaller particles are retained in the fluidized bed. The inflowing air is normally made up of the heated or unheated sizing air and the heated bottom air. The temperature of the bottom air is between 80 and 400°C and preferably between 90 and 350°C. A starting material, preferably

10 SKET granules from an earlier test batch, is advantageously introduced at the beginning of the SKET granulation process. The water from the fatty alcohol sulfate paste evaporates in the fluidized bed, resulting in the formation of partly dried to fully dried nuclei which are coated with further quantities of fatty alcohol surfactants and with olefin sulfonates, granulated and

15 again simultaneously dried. Reference is made in this connection to the teaching of German patent applications **DE 4303211 A1** and **DE 4303176 A1** of which the disclosures are hereby specifically included in the present specification.

20 Flash dryer

The simultaneous drying and granulation process may also be carried out in a horizontally arranged thin-layer evaporator with rotating internals of the type marketed, for example, by the VRV company under the name of "Flash Dryer". In simple terms, the flash dryer is a tube which can

25 be heated to different temperatures over several zones. The paste-form starting material, which is introduced by a pump, is projected onto the heated wall by one or more shafts fitted with paddles or plowshares as rotating internals and is dried on the heated wall in a thin layer typically with a thickness of 1 to 10 mm. According to the invention, it has been found to

30 be of advantage to apply a temperature gradient of 170°C (product

entrance) to 20°C (product exit) to the thin layer evaporator. To this end, the first two zones of the evaporator for example may be heated to 160°C and the last zone to 20°C. Higher drying temperatures have not been found to be of advantage in view of the thermal lability of the starting materials. The thin-layer evaporator is operated at atmospheric pressure, air being passed through in countercurrent (throughput about 50-150 m³/h). The gas entry temperature is generally in the range from 20 to 30°C while the exit temperature is in the range from 90 to 110°C.

Besides the drying and granulation of neutralized surfactant pastes, the acidic sulfonation products may also be subjected to spray neutralization as described, for example, in **EP 0319819 A1**. In this process, the acid and a highly concentrated aqueous sodium hydroxide are separately exposed to a gaseous medium, subsequently combined in stoichiometric quantities, neutralized in a multicomponent nozzle and sprayed into the dryer/granulator under a high propellant gas pressure.

One advantage of the granules is that they are not tacky and have high bulk densities of 300 to 1,200 g/l and preferably 500 to 800 g/l.

Other methods of production

Another possible method of producing the surfactant granules according to the invention is to subject the water-containing pastes of components (a) and (b) to vacuum drying. In this process, the water-containing pastes of the surfactants according to the invention, for example a 30 to 65% by weight aqueous paste, are completely concentrated by evaporation and the water-free residue is subsequently ground up into granules.

Commercial Applications

The granules according to the invention consist of components (a) and (b) in the following quantities (based on the solids component):

(a) 75 to 97, preferably 85 to 95% by weight fatty alcohol sulfate and

(b) 3 to 25, preferably 5 to 15% by weight olefin sulfonates,

with the proviso that the quantities add up to 100% by weight. The quantities shown are based on the active substance content of the components. The granules according to the invention may still contain residual quantities of water, preferably below 5% by weight, based on the granules, after the simultaneous drying and granulation process.

The solubility of the fatty alcohol sulfate granules can be considerably improved by the addition of the olefin sulfonates. Accordingly, the present invention also relates to the use of olefin sulfonates in quantities of 3 to 25% by weight for improving the solubility of fatty alcohol sulfate granules in cold water.

In another embodiment of the present invention, the olefin sulfonate/fatty alcohol sulfate granules are used for the production of laundry detergents, dishwashing detergents and cleaners. They may be present in typical quantities, preferably in the range from 0.1 to 30% by weight, based on the detergent/cleaner.

Besides the granules according to the invention, the laundry detergents, dishwashing detergents and cleaners may contain other typical ingredients such as, for example, anionic surfactants, nonionic surfactants, builders, bleaching agents, bleach activators, detergency boosters, enzymes, enzyme stabilizers, redeposition inhibitors, optical brighteners, soil repellents, foam inhibitors, inorganic salts, dyes and perfumes.

Typical examples of **anionic surfactants** are soaps, alkyl benzene sulfonates, alkane sulfonates, alkyl ether sulfonates, glycerol ether sulfonates, α -methyl ester sulfonates, sulfofatty acids, fatty alcohol ether sulfates, glycerol ether sulfates, fatty acid ether sulfates, hydroxy mixed ether sulfates, monoglyceride (ether) sulfates, fatty acid amide (ether) sulfates, mono- and dialkyl sulfosuccinates, mono- and dialkyl sulfosuccinamates, sulfotriglycerides, amide soaps, ether carboxylic acids

and salts thereof, fatty acid isethionates, fatty acid sarcosinates, fatty acid taurides, N-acyl amino acids such as, for example, acyl lactylates, acyl tartrates, acyl glutamates and acyl aspartates, alkyl oligoglucoside sulfates, protein fatty acid condensates (more particularly vegetable wheat-based products) and alkyl (ether)phosphates. Where the anionic surfactants contain polyglycol ether chains, they may have a conventional homolog distribution although they preferably have a narrow homolog distribution. Typical examples of **nonionic surfactants** are fatty alcohol polyglycol ethers, alkyl phenol polyglycol ethers, fatty acid polyglycol esters, fatty acid amide polyglycol ethers, fatty amine polyglycol ethers, alkoxyated triglycerides, mixed ethers and mixed formals, optionally partly oxidized alk(en)yl oligoglycosides and glucuronic acid derivatives, fatty acid-N-alkyl glucamides, protein hydrolyzates (more particularly vegetable wheat-based products), polyol fatty acid esters, sugar esters, sorbitan esters, polysorbates and amine oxides. Where the nonionic surfactants contain polyglycol ether chains, they may have a conventional homolog distribution although they preferably have a narrow homolog distribution.

A suitable **solid builder** is, in particular, finely crystalline zeolite containing synthetic and bound water, such as detergent-quality zeolite NaA. However, zeolite NaX and mixtures of NaA and NaX are also suitable. The zeolite may be used in the form of a spray-dried powder or even as an undried stabilized suspension still moist from its production. Where the zeolite is used in the form of a suspension, the suspension may contain small additions of nonionic surfactants as stabilizers, for example 1 to 3% by weight – based on zeolite – of ethoxylated C₁₂₋₁₈ fatty alcohols containing 2 to 5 ethylene oxide groups or ethoxylated isotridecanols. Suitable zeolites have a mean particle size of less than 10 µm (volume distribution, as measured by the Coulter Counter Method) and contain preferably 18 to 22% by weight and more preferably 20 to 22% by weight of bound water. Suitable substitutes or partial substitutes for zeolites are

crystalline layer-form sodium silicates with the general formula $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$, where M is sodium or hydrogen, x is a number of 1.9 to 4 and y is a number of 0 to 20, preferred values for x being 2, 3 or 4. Crystalline layer silicates such as these are described, for example, in

5 European patent application **EP 0 164 514 A**. Preferred crystalline layer silicates are those in which M in the general formula stands for sodium and x assumes the value 2 or 3. Both β - and γ -sodium disilicates $\text{Na}_2\text{Si}_2\text{O}_5\cdot y\text{H}_2\text{O}$ are particularly preferred, β -sodium disilicate being obtainable for example by the process described in International patent

10 application **WO 91/08171**. The powder form detergents according to the invention preferably contain 10 to 60% by weight of zeolite and/or crystalline layer silicates as solid builders, mixtures of zeolite and crystalline layer silicates in any ratio being particularly advantageous. In one particularly preferred embodiment, the detergents contain 20 to 50%

15 by weight of zeolite and/or crystalline layer silicates. Particularly preferred detergents contain up to 40% by weight of zeolite and, more particularly, up to 35% by weight of zeolite, based on water-free active substance. Other suitable ingredients of the detergents are water-soluble amorphous silicates which are preferably used in combination with zeolite and/or

20 crystalline layer silicates. Particularly preferred detergents are those which contain above all sodium silicate with a molar ratio of Na_2O to SiO_2 (modulus) of 1:1 to 1:4.5 and preferably 1:2 to 1:3.5. The amorphous sodium silicate content of the detergents is preferably up to 15% by weight and more preferably from 2 to 8% by weight. Phosphates, such as

25 tripolyphosphates, pyrophosphates and orthophosphates, may also be present in the detergents in small quantities. The phosphate content of the detergents is preferably up to 15% by weight and, more particularly, from 0 to 10% by weight. In addition, the detergents may contain layer silicates of natural and synthetic origin. Corresponding layer silicates are known, for

30 example, from patent applications **DE 23 34 899 B**, **EP 0 026 529 A** and

DE 35 26 405 A. Their suitability for use is not confined to a particular composition or structural formula. However, smectites are preferred, bentonites being particularly preferred. Suitable layer silicates which belong to the group of water-swellaible smectites are, for example, those

5 corresponding to the following general formulae:

$(\text{OH})_4\text{Si}_{8-y}\text{Al}_y(\text{Mg}_x\text{Al}_{4-x})\text{O}_{20}$ montmorillonite

$(\text{OH})_4\text{Si}_{8-y}\text{Al}_y(\text{Mg}_{6-z}\text{Li}_z)\text{O}_{20}$ hectorite

$(\text{OH})_4\text{Si}_{8-y}\text{Al}_y(\text{Mg}_{6-z}\text{Al}_z)\text{O}_{20}$ saponite

10

where $x = 0$ to 4 , $y = 0$ to 2 and $z = 0$ to 6 . In addition, small quantities of iron may be incorporated in the crystal lattice of the layer silicates corresponding to the above formulae. By virtue of their ion-exchanging properties, the layer silicates may also contain hydrogen, alkali metal and

15 alkaline earth metal ions, more particularly Na^+ and Ca^{2+} . The quantity of water of hydration is generally in the range from 8 to 20% by weight and is dependent upon the degree of swelling and upon the processing method.

Suitable layer silicates are known, for example, from **US 3,966,629**, **US 4,062, 647**, **EP 0 026 529 A** and **EP 0 028 432 A**. Layer silicates which

20

have been substantially freed from calcium ions and strongly coloring iron ions by an alkali treatment are preferably used. Useful organic builders are, for example, the polycarboxylic acids preferably used in the form of their sodium salts, such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids, aminocarboxylic acids, nitrilotriacetic acid (NTA), providing their use is not ecologically unsafe, and mixtures thereof. Preferred salts are the salts of polycarboxylic acids, such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids and mixtures thereof. Suitable polymeric polycarboxylates are, for

25

example, the sodium salts of polyacrylic acid or polymethacrylic acid, for

30 example those with a relative molecular weight of 800 to 150,000 (based

on acid). Suitable copolymeric polycarboxylates are, in particular, those of acrylic acid with methacrylic acid and acrylic acid or methacrylic acid with maleic acid. Copolymers of acrylic acid with maleic acid which contain 50 to 90% by weight of acrylic acid and 50 to 10% by weight of maleic acid are particularly suitable. Their relative molecular weight, based on free acids, is generally in the range from 5,000 to 200,000, preferably in the range from 10,000 to 120,000 and more preferably in the range from 50,000 to 100,000. It is not absolutely essential to use polymeric polycarboxylates. However, if polymeric polycarboxylates are used, detergents containing biodegradable polymers, for example terpolymers which contain acrylic acid and maleic acid or salts thereof and vinyl alcohol or vinyl alcohol derivatives as monomers or acrylic acid and 2-alkyl allyl sulfonic acid or salts thereof and sugar derivatives as monomers are preferred. The terpolymers obtained in accordance with the teaching of German patent applications **DE 42 21 381 A** and **DE 43 00 772 A** are particularly preferred. Other suitable builders are polyacetals which may be obtained by reacting dialdehydes with polyol carboxylic acids containing 5 to 7 carbon atoms and at least 3 hydroxyl groups, for example as described in European patent application **EP 0 280 223 A**. Preferred polyacetals are obtained from dialdehydes, such as glyoxal, glutaraldehyde, terephthalaldehyde and mixtures thereof and from polyol carboxylic acids, such as gluconic acid and/or glucoheptonic acid.

Among the compounds yielding hydrogen peroxide in water which are used as **bleaching agents**, sodium perborate tetrahydrate and sodium perborate monohydrate are particularly important. Other suitable bleaching agents are, for example, peroxycarbonate, citrate perhydrates and salts of peracids, such as perbenzoates, peroxyphthalates or diperoxydodecanedioic acid. They are normally used in quantities of 8 to 25% by weight. Sodium perborate monohydrate is preferred and is used in quantities of 10 to 20% by weight and preferably in quantities of 10 to 15% by weight. By

virtue of its ability to bind free water to form the tetrahydrate, it contributes towards increasing the stability of the detergent.

In order to obtain an improved bleaching effect where washing is carried out at temperatures of 60°C or lower, **bleach activators** may be incorporated in the preparations. Examples of bleach activators are N-acyl and O-acyl compounds which form organic peracids with hydrogen peroxide, preferably N,N'-tetraacylated diamines, also carboxylic anhydrides and esters of polyols, such as glucose pentaacetate. The bleach activator content of bleach-containing detergents is in the usual range, i.e. preferably between 1 and 10% by weight and more preferably between 3 and 8% by weight. Particularly preferred bleach activators are N,N,N',N'-tetraacetyl ethylenediamine and 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine.

Suitable **enzymes** are those from the class of proteases, lipases, amylases, cellulases and mixtures thereof. Enzymes obtained from bacterial strains or fungi, such as *Bacillus subtilis*, *Bacillus licheniformis* and *Streptomyces griseus*, are particularly suitable. Proteases of the subtilisin type are preferably used, proteases obtained from *Bacillus lentus* being particularly preferred. They may be used in quantities of about 0.2 to about 2% by weight. The enzymes may be adsorbed onto supports and/or embedded in shell-forming materials to protect them against premature decomposition. In addition to the monohydric and polyhydric alcohols and the phosphonates, the detergents may contain other enzyme stabilizers. For example, 0.5 to 1% by weight of sodium formate may be used. It is also possible to use proteases which are stabilized with soluble calcium salts and which have a calcium content of preferably about 1.2% by weight, based on the enzyme. However, it is of particular advantage to use boron compounds, for example boric acid, boron oxide, borax and other alkali metal borates, such as the salts of orthoboric acid (H_3BO_3), metaboric acid (HBO_2) and pyroboric acid (tetraboric acid $H_2B_4O_7$).

The function of **red deposition inhibitors** is to keep the soil detached from the fibers suspended in the wash liquor and thus to prevent discoloration. Suitable redeposition inhibitors are water-soluble, generally organic colloids, for example the water-soluble salts of polymeric carboxylic acids, glue, gelatin, salts of ether carboxylic acids or ether sulfonic acids of starch or cellulose or salts of acidic sulfuric acid esters of cellulose or starch. Water-soluble polyamides containing acidic groups are also suitable for this purpose. Soluble starch preparations and other starch products than those mentioned above, for example degraded starch, aldehyde starches, etc., may also be used. Polyvinyl pyrrolidone is also suitable. However, cellulose ethers, such as carboxymethyl cellulose, methyl cellulose, hydroxyalkyl cellulose, and mixed ethers, such as methyl hydroxyethyl cellulose, methyl hydroxypropyl cellulose, methyl carboxymethyl cellulose and mixtures thereof, and polyvinyl pyrrolidone are preferably used, for example in quantities of 0.1 to 5% by weight, based on the detergent.

The detergents may contain derivatives of diaminostilbene disulfonic acid or alkali metal salts thereof as **optical brighteners**. Suitable optical brighteners are, for example, salts of 4,4'-bis-(2-anilino-4-morpholino-1,3,5-triazinyl-6-amino)-stilbene-2,2'-disulfonic acid or compounds of similar structure which, instead of the morpholino group, contain a diethanolamino group, a methylamino group, an anilino group or a 2-methoxyethylamino group. Brighteners of the substituted diphenyl styryl type, for example alkali metal salts of 4,4'-bis-(2-sulfostyryl)-diphenyl, 4,4'-bis-(4-chloro-3-sulfostyryl)-diphenyl or 4-(4-chlorostyryl)-4'-(2-sulfostyryl)-diphenyl, may also be present. Mixtures of the brighteners mentioned above may also be used. Uniformly white granules are obtained if, in addition to the usual brighteners in the usual quantities, for example between 0.1 and 0.5% by weight and preferably between 0.1 and 0.3% by weight, the detergents also contain small quantities, for example 10^{-6} to $10^{-3}\%$ by weight and preferably

around 10⁻⁵% by weight, of a blue dye. A particularly preferred dye is Tinolux® (a product of Ciba-Geigy).

Suitable **soil repellents** are substances which preferably contain ethylene terephthalate and/or polyethylene glycol terephthalate groups, the
5 molar ratio of ethylene terephthalate to polyethylene glycol terephthalate being in the range from 50:50 to 90:10. The molecular weight of the linking polyethylene glycol units is more particularly in the range from 750 to 5,000, i.e. the degree of ethoxylation of the polymers containing poly-
ethylene glycol groups may be about 15 to 100. The polymers are
10 distinguished by an average molecular weight of about 5,000 to 200,000 and may have a block structure, but preferably have a random structure. Preferred polymers are those with molar ethylene terephthalate: polyethylene glycol terephthalate ratios of about 65:35 to about 90:10 and preferably in the range from about 70:30 to 80:20. Other preferred
15 polymers are those which contain linking polyethylene glycol units with a molecular weight of 750 to 5,000 and preferably in the range from 1,000 to about 3,000 and which have a molecular weight of the polymer of about 10,000 to about 50,000. Examples of commercially available polymers are the products Milease® T (ICI) or Repelotex® SRP 3 (Rhône-Poulenc).

20 Where the detergents are used in washing machines, it can be of advantage to add conventional **foam inhibitors** to them. Suitable foam inhibitors are, for example, soaps of natural or synthetic origin which have a high percentage of C₁₈₋₂₄ fatty acids. Suitable non-surface-active foam
inhibitors are, for example, organopolysiloxanes and mixtures thereof with
25 microfine, optionally silanized silica and paraffins, waxes, microcrystalline waxes and mixtures thereof with silanized silica of bis-stearyl ethylenediamide. Mixtures of various foam inhibitors, for example mixtures of silicones, paraffins or waxes, may also be used with advantage. The
foam inhibitors, more particularly silicone- or paraffin-containing foam
30 inhibitors, are preferably fixed to a granular water-soluble or water-

dispersible carrier/support. Mixtures of paraffins and bis-stearyl ethylenediamides are particularly preferred.

Examples

Example 1.

Water-containing pastes of C_{16/18} fatty alcohol sulfates and various quantities of α -olefin sulfonate [sodium olefin sulfonate (C₁₄₋₁₆), Elfan® OS 46, Azko Nobel, 1] C_{12/14} fatty alcohol sulfate sodium salt (**C1**) and ocnol sulfate sodium salt (**C2**) were subjected to vacuum drying and then ground into granules. The solubility of these granules was tested in a hand washing test and the residue in % by weight was determined (Table 1). Even when added to the C_{16/18} fatty alcohol sulfate in a quantity of 5%, the α -olefin sulfonate improves its dissolving and dispersing behavior by comparison with **C1** and **C2**.

Table 1.

Solubility of C_{16/18} fatty alcohol in the hand washing test (% by weight residue)

Addition (% by wt.)	1 α -Olefin sulfonate	C1 C _{12/14} Fatty alcohol sulfate sodium salt	C2 Ocnol sulfate sodium salt
5	6.6	37.4	32.4
10	4.4	37.0	32.2
15	9.0*)	36.7	28.0

*) The results can be falsified by gelation

Example 2.

Starting materials

- (a) C_{16/18} fatty alcohol sulfate Sulfopon® T 55 (51.5% by weight active substance)
- (b) α -Olefin sulfonate Elfan® OS 46 (37.0% by weight active substance)

(c) C_{12/14} fatty alcohol sulfate Texapon® LS 35 (35.2% by weight active substance)

(d) Ocenol sulfate sodium salt (59.7% by weight active substance)

Table 2.

Concentrations of the water-containing pastes used (% by weight)

Composition	1	2	3	C1	C2	C3	C4	C5	C6
(a) + (b)	93.1 8 6.82	86.60 13.40	80.28 19.72	-	-	-	-	-	-
(a) + (c)	-	-	-	92.85 7.15	86.02 13.98	79.48 20.52	-	-	-
(a) + (d)	-	-	-	-	-	-	95.65 4.35	91.25 8.75	86.77 13.23
Paste concentration	50.5 1	49.56	48.64	50.33	49.22	48.16	51.86	52.22	52.28
Percentage (b) of paste	5	10	15	-	-	-	-	-	-
Percentage (c) of paste	-	-	-	5	10	15	-	-	-
Percentage (d) of paste	-	-	-	-	-	-	5	10	15

Production of the granules in a fluidized bed

Water-containing pastes **1** to **3** according to the invention and comparison pastes **C1** to **C6** were sprayed into the fluidized bed in various test batches.

Process parameters:

Feed air: 720 to 750 Nm/h

Feed air temperature: 140 to 150°C

Air exit temperature: 80 to 85°C

Quantity sprayed: 21 to 30 kg/h

Exhaust air: 120 to 130 Nm/h

Duration of test: 4 h

Quantity of product: 15 kg

Surfactant granules with the following characteristics were obtained:

Bulk density:	500 to 650 g/l
Active substance content:	88 to 97%
Residual moisture:	2.0 to 3.0%

5

Solubility test:

The solubility of the granules obtained (**1**, **C1** and **C4**) was tested in a hand washing test and the residue was determined. Surfactant granules which contain 5% by weight α -olefin sulfonate in addition to 95% by weight

10 C_{16/18} fatty alcohol sulfate (**1**) show improved solubility (residue: 7.0% by weight) by comparison with granules containing 5% by weight of C_{12/14} fatty alcohol sulfate (**C1**, residue: 40.0% by weight) or oenol sulfate sodium salt (**C4**, residue: 35.0% by weight).

CLAIMS

1. Surfactant granules consisting of
- (a) 75 to 97% by weight of fatty alcohol sulfates and
- (b) 3 to 25% by weight of olefin sulfonates,
- 5 with the proviso that the quantities add up to 100% by weight.

2. Surfactant granules as claimed in claim 1, characterized in that they contain as component (a) fatty alcohol sulfates corresponding to formula (I):



in which R^1 is a linear or branched, saturated or unsaturated hydrocarbon radical containing 6 to 18 carbon atoms and X is an alkali metal or alkaline earth metal, ammonium, alkyl ammonium, alkanolammonium or glucammonium.

3. Surfactant granules as claimed in claims 1 and/or 2, characterized in that they contain as component (b) olefin sulfonates obtained by addition of SO_3 onto olefins corresponding to formula (II):



in which R^2 and R^3 independently of one another represent H or alkyl groups containing 1 to 20 carbon atoms, with the proviso that R^2 and R^3 together contain at least 6 and preferably 10 to 16 carbon atoms,

25 and subsequent hydrolysis and neutralization.

4. Surfactant granules as claimed in at least one of claims 1 to 3, characterized in that they contain as component (b) olefin sulfonates which consist of ca. 60% by weight of alkane sulfonates and ca. 40% by weight of hydroxyalkane sulfonates, of which 80 to 85% by weight are mono-sulfonates and 15 to 20% by weight disulfonates.

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5. Surfactant granules as claimed in at least one of claims 1 to 4, characterized in that they consist of

(a) 85 to 95% by weight of fatty alcohol sulfates and

(b) 5 to 15% by weight of olefin sulfonates,

5 with the proviso that the quantities add up to 100% by weight.

6. A process for the production of the surfactant granules claimed in claim 1, characterized in that a water-containing paste of component (a) is simultaneously dried and granulated in the presence of component (b).

7. A process as claimed in claim 6, characterized in that granulation is
10 carried out in a fluidized bed.

8. The use of olefin sulfonates in quantities of 3 to 25% by weight for improving the solubility of fatty alcohol sulfate granules in cold water.

9. The use of the olefin sulfonate/fatty alcohol sulfate granules claimed
15 in claim 1 for the production of laundry detergents, dishwashing detergents and cleaners.

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			First Named Inventor	KISCHKEL, Ditmar
			COMPLETE IF KNOWN	
			Application Number	09/868,549
			Filing Date	08/07/01
			Group Art Unit	
			Examiner Name	

As a below named inventor, I hereby declare that

My residence, post office address, and citizenship are as stated below next to my name

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

TENSIDE GRANULATES

(Title of the invention)

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) 12/10/1999 as United States Application Number or PCT International

Application Number PCT/EP99/09739 and was amended on (MM/DD/YYYY) (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

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			Not Claimed		YES	NO
198 58 886.0	Germany	12/19/1998	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
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DECLARATION

Page 2

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U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
	PCT/EP99/09739 ✓	12/10/1999 ✓	

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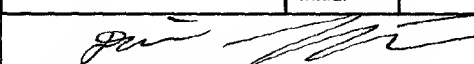
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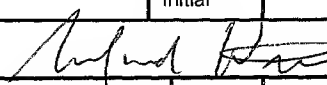
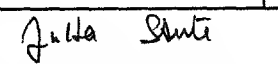
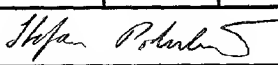
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